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PATUXENT RIVER, MARYLAND 20670-5304



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HIGH-PERFORMANCE, LOW VOLATILE ORGANIC COMPOUND CONTENT EPOXY SYSTEMS FOR NAVAL AIRCRAFT COATINGS

by

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28 December 1995

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ABSTRACT

New environmental regulations have prompted the need for organic coatings with low volatile organic compound (VOC) levels that maintain the properties of their high VOC counterparts. Loss of solvents creates such problems as poor film formation and high application viscosity. The effects of low molecular weight polymers and reactive diluents in coating formulations were studied with respect to properties deemed essential for overall operational readiness of naval aircraft. Such materials were incorporated into a compliant, high-gloss epoxy topcoat. While attempts to improve the properties of the topcoat under extreme conditions were unsuccessful, the new system met all the requirements of MIL-C-22750, the Military Specification for an epoxy topcoat. The coating also exceeded the performance of the control formulation in many categories, including a reduction of VOC's by 40%.

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CONTENTS

	<u>Page No.</u>
ABSTRACT	ii
ACKNOWLEDGMENT	ii
FIGURES.....	iv
TABLES	iv
 SUMMARY.....	1
 INTRODUCTION	1
BACKGROUND.....	1
APPROACH	2
HIGH-SOLIDS SOLVENTBORNE COATINGS	3
 EXPERIMENTAL PROCEDURE	6
HIGH-SOLIDS EPOXY TOPCOATS.....	6
MATERIALS	6
EPOXY FORMULATION TECHNIQUES.....	6
TESTING	8
 RESULTS AND DISCUSSION.....	9
 REFERENCES	13
 DISTRIBUTION.....	15

FIGURES

	<u>Page No.</u>
1. REDUCTION OF MOLECULAR WEIGHT OR ADDITION OF SOLVENT.....	4
WILL SHIFT TG TO LOWER TEMPERATURES SO THAT THE FREE VOLUME AT THE TEMPERATURE OF VISCOSITY MEASUREMENT WILL BE LARGER	
2. CHEMICAL STRUCTURE OF A STANDARD DGEBA-BASED EPOXY RESIN	5
3. THE CHEMICAL STRUCTURE OF A TYPICAL DGEBF RESIN	5
4. STRUCTURES OF MONOFUNCTIONAL EPOXIDE REACTIVE DILUENTS	9
5. STRUCTURE OF THE DIFUNCTIONAL REACTIVE DILUENT NGDE.....	10

TABLES

	<u>Page No.</u>
1. MATERIALS USED FOR FORMULATING LOW VOC EPOXY TOPCOATS	7
2. SAMPLE EPOXY TOPCOAT FORMULATION	8
3. TESTING RESULTS (MIL-C-22750) FOR EPOXY TOPCOATS A, B, C	11
AND CONTROL	

SUMMARY

New environmental regulations have prompted the need for development of organic coatings with low volatile organic compound (VOC) content that maintains the performance properties of their high VOC counterparts. The objective of this work is to develop low VOC coatings for use on naval aircraft and ground support equipment. Through the use of high-solids resins and reactive diluents, a VOC-compliant epoxy topcoat has been developed. This topcoat exhibited superior performance to any other epoxy topcoat system developed in this laboratory to date, including the low-solids control formulation.

INTRODUCTION

BACKGROUND

The primary defense against environmental degradation is the organic coating system. High performance coatings are essential to the overall operational readiness of naval aircraft. New environmental regulations, particularly on the west coast, have prompted the need for development of organic coatings with low VOC levels that maintain the performance properties of their high VOC counterparts.

The objective of this study is to develop low VOC content polymer systems for formulation of high performance, low VOC epoxy and polyurethane coatings for use on naval aircraft and ground support equipment. These new coating systems must satisfy the high performance requirements on a variety of substrates and in application conditions including the severe environment of Navy operations (water, salt, and humidity). Recent advances in low VOC technology permit the development of UV stable epoxy coatings based on reactive diluents and polyurethane coatings with a minimum of 50% reduction of VOC from current high-solids urethane topcoats. Water-based technology permits the development of high performance coatings from water-reducible or water-based resins. The corrosion resistance, physical performance properties, and VOC content of current aircraft primers and topcoats will be used as parameters in developing protective coatings from the best materials.

The Environmental Protection Agency (EPA), by enforcing the Clean Air Act, has tried to standardize organic emission regulations for paint application in the aerospace industry. The most stringent regulations in the United States are in effect in California because of severe air-quality problems. Aircraft and the weapons attached to them fall under specific aerospace rules that limit the amount of VOC in the paints at the point of application.¹

VOC's are defined in California Rule 1124 - Aerospace Assembly and Component Coating Operations.² Grams of VOC per liter of coating (g/l), less water and exempt compounds, is the weight of VOC per combined volume of VOC and coating solids. It is calculated using equation 1.

$$VOC = \frac{W_s - W_w - W_{es}}{V_m - V_w - V_{es}} \quad (1)$$

where: W_s = weight of volatile compounds in grams
 W_w = weight of water in grams
 W_{es} = weight of exempt compounds in grams
 V_m = volume of materials in liters
 V_w = volume of water in liters
 V_{es} = volume of exempt compounds in liters

The current maximum limits for aerospace primers and topcoats are 350 and 420 g/l, respectively. Measurements of VOC content must include not only solvents but any volatile chemicals in the resin, pigment, or additives of the paint. Exempt solvents, such as water, are not included in the volatile content or the total paint volume. The most common test method for VOC measurement is ASTM D 3960.

In the past, the VOC content in a unit volume of a paint formulation was not considered an important issue in the industry. Over the years, new regulations have made the VOC level a major requirement to the paint industry and to the Navy; these restrictions to reduce the high levels of VOC in low solids formulations have been a continuous challenge.^{3,4,5,6} The paint industry has responded to these regulations by either controlling the solvents from entering the environment or designing formulations with fewer solvents.

Less solvent in a formulation results in higher paint viscosities and poorer film forming capabilities because of the material's incapability to flow, therefore, implying that extra demands be added to the requirements of processing and quality controls.^{7,8} This could be achieved by using solvents having high dilution effects or reducing resin molecular weight. The lower molecular weight resins generally have a greater number of solvents capable of dissolving them and possible combinations of solvents would be readily available. Considerable contributions have been made to solvent technology in minimizing the VOC limit. It has created a tremendous challenge for the coatings industry to meet the low VOC restrictions while maintaining conventional resin system performance properties. This challenge is especially evident in ambient temperature curing systems.

APPROACH

Exploration has begun into different types of coatings that contain less solvents than the conventional low solids formulations.⁹ Getting the solvent out of the paint system means either using binders that will function as carriers with little or no solvent, or using water as the dispersion medium. Therefore, the technologies receiving the most attention are high-solids solventborne formulations and waterborne formulations; the former technology will be the crux of this paper.

A third technology, now used to a lesser extent, is exempt solvent technology. 1,1,1-trichloroethane (TCA) is listed as an exempt solvent in VOC regulations issued by many states.¹ Since it is not photochemically reactive, it does not contribute to the generation of smog in industrial areas. However, if it reaches the upper atmosphere, TCA will react with and degrade the ozone layer.¹⁰ For this reason, and the fact that chlorinated solvents are treated as a hazardous waste requiring expensive disposal methods, the future of exempt solvent technology is limited. Therefore, this approach was not pursued in this investigation.

HIGH-SOLIDS SOLVENTBORNE COATINGS

Some difficulties have been encountered in meeting performance requirements with high-solids coatings. Reduced solvent concentrations generally yield a higher viscosity, shorter pot life, and rougher surface finish.^{1,11} Pot life and surface finish can be adjusted by the use of different additives without significantly affecting performance properties. It is the reduction of coating viscosity where the majority of effort is taking place.

High-solids content in coatings can be achieved in various ways. One such way is through the use of "blocked" polymers, where one reactant is chemically modified to be stable when packaged with its coreactant. When the coating is applied, the modified reactant becomes "unblocked" by reaction with atmospheric moisture or the application of heat. However, during unblocking, a ketone or aldehyde is generated, which contributes to VOC's. Elevated cure temperatures are also undesirable for aircraft repair applications. Another approach is through the use of less solvent, but, as discussed earlier, this method leads to poor film-forming capabilities. The most effective method of producing a high-solids content is the use of low molecular weight oligomers as the components of the resin.¹² High-solids coatings are frequently based on the same polymer types used in conventional systems, but with reduced molecular weight.

The fact that the molecular weight reduction helps to achieve application viscosity at high solids is clarified by the physical description of flow associated with the free volume concept. The molecular weight reduction causes an increase in free volume because the chain ends undergo segmental motion relatively easily. Figure 1¹³ shows that free volume increases above T_g. The increase is attributed to the segmental motion that creates submicroscopic voids.^{13,14} With the added volume, polymer chains can move past each other more easily, resulting in a lower resin viscosity.

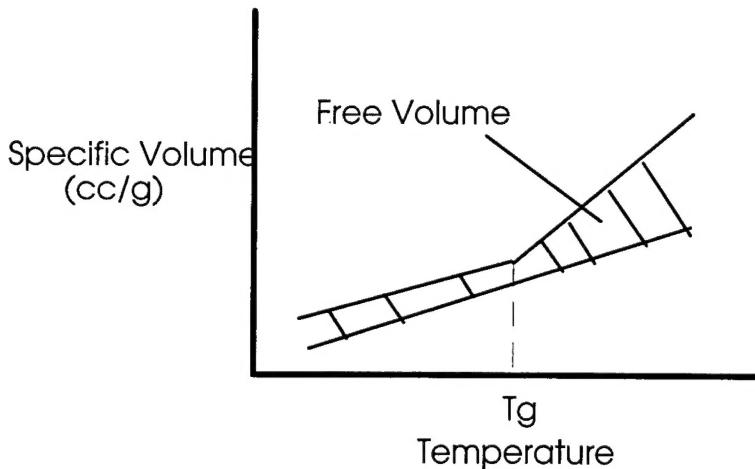


Figure 1

REDUCTION OF MOLECULAR WEIGHT OR ADDITION OF SOLVENT WILL SHIFT TG TO LOWER TEMPERATURES SO THAT THE FREE VOLUME AT THE TEMPERATURE OF VISCOSITY MEASUREMENT WILL BE LARGER¹³

Another approach to reducing coating viscosity is through the use of reactive diluents. Reactive diluents are low molecular weight oligomers that act as a "solvent" for a viscous resin in a two-component system. Not only do they reduce the resin viscosity, but they also act as a replacement for some of the added solvent. During the curing process, the reactive diluent becomes part of the polymer chain. It is not driven off as a solvent and, as a result, is not considered a VOC.

Epoxy resins are among the binders that allow the formulation of high-solids paints. For more than 30 years, epoxy/polyamide systems have been used as the standard binder for coatings requiring superior chemical and corrosion resistance. The performance standard for these coatings utilizes an epoxy resin, cured with a standard high-viscosity polyamide curing agent. The epoxy resin is based on the glycidyl ether of bisphenol-A (DGEBA); its structure is given in figure 2. Here, the value of "n" is between 2 and 3, and the epoxide equivalent weight (molecular weight divided by functionality) is approximately 500. In formulations containing such systems, 40-50 volume percentage solvent is necessary to attain a sprayable viscosity, significantly contributing to VOC.

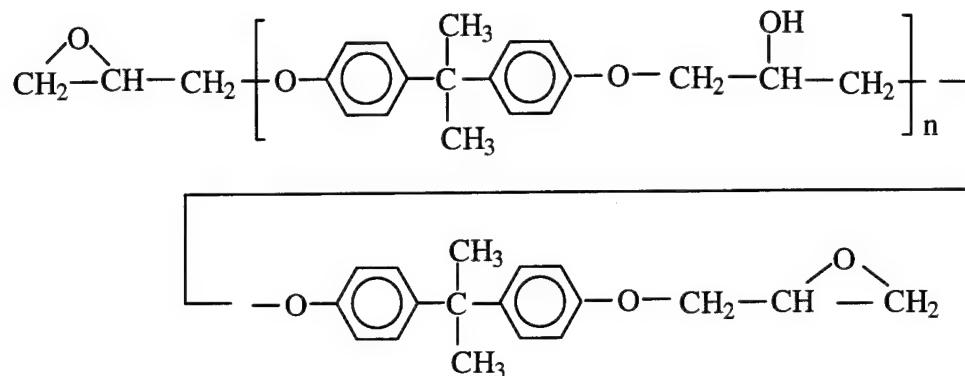


Figure 2
CHEMICAL STRUCTURE OF A STANDARD DGEBA-BASED EPOXY RESIN

VOC reduction was attained as follows. First, the standard resin was replaced with lower-molecular weight resins (therefore, lower equivalent weight). These new resins are based on modified versions of DGEBA, where the "n" values are between 1 and 2.¹⁵ The decrease in molecular weight results in resins with lower viscosities, as described earlier in this document. Other resins are based on the glycidyl ether of bisphenol-F (DGEBF); its structure is given in figure 3. Its similar structure to DGEBA dictates that DGEBF's performance properties should closely resemble DGEBA's. However, replacement of the methyl groups with hydrogens results in added chain segment motions, which ultimately yields a resin with a lower viscosity than the standard.¹⁶ Second, some of the solvent was replaced by a reactive diluent. Reactive are low molecular weight epoxide compounds^{17,18} that react with the curing agent and become part of the polymer backbone.

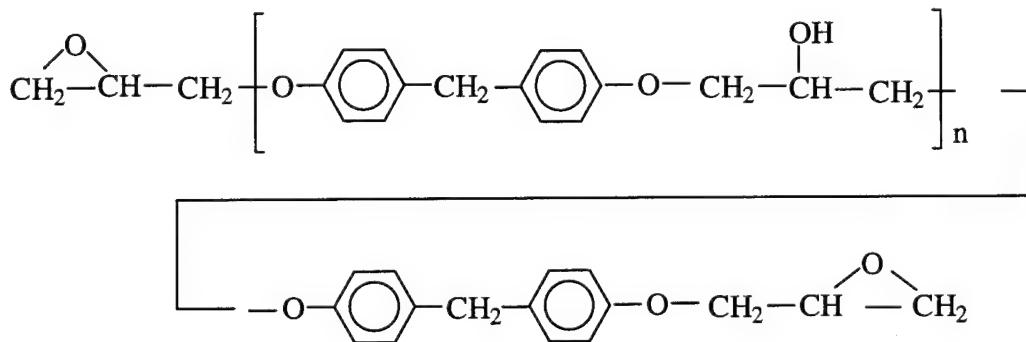


Figure 3
THE CHEMICAL STRUCTURE OF A TYPICAL DGEBF RESIN

EXPERIMENTAL PROCEDURE

HIGH-SOLIDS EPOXY TOPCOATS

MATERIALS

Epoxy topcoats were formulated from the list of ingredients given in table 1. Table 1 specifies each ingredient's classification, manufacturer, equivalent weight of solution in grams per epoxide (if applicable), solids content in percent, density in pounds per gallon, and reason for incorporation into the formulation. A standard epoxy topcoat, with a VOC of 565 g/l, was used as the control. A sample epoxy topcoat formulation is given in table 2.

EPOXY FORMULATION TECHNIQUES

The order of addition is crucial in these new formulations. Component I for the epoxy coatings was prepared as follows. The resin and diluent were introduced into a Nalgene® jar, followed by the pigment dispersant. If Tint-Ayd ST 8003® was used, a pigment dispersant was not required because this material is predispersed. Then, the other additives were incorporated, except for the surfactant. The solvent was introduced and, finally, the surfactant was added. To this mixture, an approximately equal volume of 6 mm glass beads was placed into the jar. The jar was placed on a paint mixer and shaken for 30 min to achieve the proper pigment grind. If Tint-Ayd ST 8003® was used as the pigment, the mixture was shaken for 5 min without the glass beads. The final mixtures were filtered and stored under ambient laboratory conditions until use. Component II was used as received from the manufacturer.

Table 1
MATERIALS USED FOR FORMULATING LOW VOC EPOXY TOPCOATS

Material	Manufacturer	Equivalent Wt. (g)	Solids (%)	Density (lb/gal)	Purpose
<u>Resins</u>					
Epon 836-C-75	Shell Chemicals	410	75	8.90	DGEBA Binder
DER 660-PA80	Dow Chemicals	406.25	80	9.33	DGEBA Binder
Epon 861	Shell Chemicals	159	100	9.68	DGEBF Binder
<u>Diluents</u>					
Allyl glycidyl ether (AGE)	Ageflex	117.50	100	8.09	Reactive diluent/binder
Butyl glycidyl ether (BGE)	Ageflex	139.50	100	7.67	Reactive diluent/binder
Cresyl glycidyl ether (CGE)	Pacific Anchor Chemicals	182.50	100	9.01	Reactive diluent/binder
Neopentyl glycol diglycidyl ether (NGDE)	Air Products and Chemicals	137.50	100	8.75	Reactive diluent/binder
NC-513LC	Cardolite Corp.	425	100	8.20	High equiv. wt. reactive dil. / binder
<u>Pigments</u>					
Ti-Pure R960	DuPont	N/A	100	32.53	TiO ₂
Tint-Ayd ST 8003	Daniel Products	N/A	80	15.80	TiO ₂ dispersion
<u>Additives</u>					
Fluorad FC-430	3M	N/A	99	9.57	Surfactant
Nuosperse 657	Hüls America	N/A	73	7.84	Pigment dispersant
Tinuvin 292	Ciba-Geigy	N/A	100	8.27	Hindered amine light stabilizer
Tinuvin 328	Ciba-Geigy	N/A	100	9.75	UV absorber
<u>Solvent</u>					
PM glycol ether	Arco Chemicals	N/A	0	7.64	Propylene glycol, methyl ether solvent
<u>Curing Agents</u>					
Epi-Cure 3140	Shell Chemicals	95	100	8.10	Binder crosslinker
NC-541X90	Cardolite Corp.	144.44	90	8.16	Binder crosslinker

Table 2
SAMPLE EPOXY TOPCOAT FORMULATION

Raw Material	Weight (lb)	Volume (gal)	Weight Solids (%)	Volume Solids (%)
<u>Component I:</u>				
Epon 836-C-75	85.00	9.55	63.75	6.36
NGDE	51.00	5.83	51.00	5.83
Tint-Ayd ST 8003	186.16	11.78	148.93	6.93
Tinuvin 292	3.64	0.44	3.64	0.44
Tinuvin 328	3.64	0.37	3.64	0.37
FC-430	1.42	0.15	1.41	0.15
PM glycol ether	78.97	10.34	0.00	0.00
<u>Component II:</u>				
Epi-Cure 3140	80.95	9.99	80.95	9.99
Wt. Solids = 72%	Vol. Solids = 62%	PVC = 23.8% Curing Agent: Epoxy Ratio = 1.47	Lbs / gal. = 10.13	VOC = 340 g/l

TESTING

The tests used to evaluate the epoxy topcoats are specified in MIL-C-22750, the Navy's specification for a compliant, low-VOC epoxy topcoat. These tests include adhesion, water/fluid resistance, flexibility, and measurement of miscellaneous properties such as admix viscosity, pot life, gloss, weatherability, etc. In most cases, more severe versions of specification tests were conducted to ascertain coating limits (e.g., adhesion after exposure to water at 150°F for 7 days). Nonspecification tests performed were impact elongation for flexibility (GE impact; FED-STD-141, Test Method No. 6226)¹⁹ and cleanability.²⁰

Aluminum panels for testing are specified in MIL-C-22750. These panels were wiped with methyl ethyl ketone to remove any surface contaminants before use. All panels except for those used in weathering and flexibility tests were coated by conventional spray with MIL-P-23377 epoxy-polyamide primer to a thickness of 0.6-0.9 mils. After mixing components I and II of the topcoat, an induction time of 30 min was allowed for reaction to begin. The topcoat was applied by conventional spray to a thickness of about 2 mils within 2 hr of primer application. All panels were allowed to cure at ambient laboratory conditions for 2 weeks prior to evaluation.

RESULTS AND DISCUSSION

To formulate compliant epoxy topcoats with viscosities low enough to be applied by conventional spray techniques (approximately 30 sec through a No. 4 Ford cup, or about 100 cps), reactive diluents had to be used in diluent:epoxy resin ratios as high as 44% (based on solids). This amount more than doubles the manufacturer's suggested usage of 20%. It was therefore imperative that the diluent be compatible with the other ingredients in the formulation and that epoxy coatings containing the diluent exhibited no significant loss of protection properties when tested and compared to the high-VOC standard system.

Early formulations incorporated monofunctional epoxide reactive diluents into the epoxy topcoats; their structures are shown in figure 4. These materials are the most common reactive diluents for epoxy systems and are readily available from commercial sources. All coatings containing these monofunctional diluents performed better than the in-house standard; however, incompatibilities between the diluents and other constituents were noticed, especially in those topcoats prepared with AGE and BGE. After weathering for 500 hr in a xenon-arc lamp Weatherometer and even on exposure to ambient laboratory conditions for several weeks, an oily substance was present on the paint film. This substance significantly reduced gloss and solvated the artificial soil used in cleanability tests, resulting in low values.

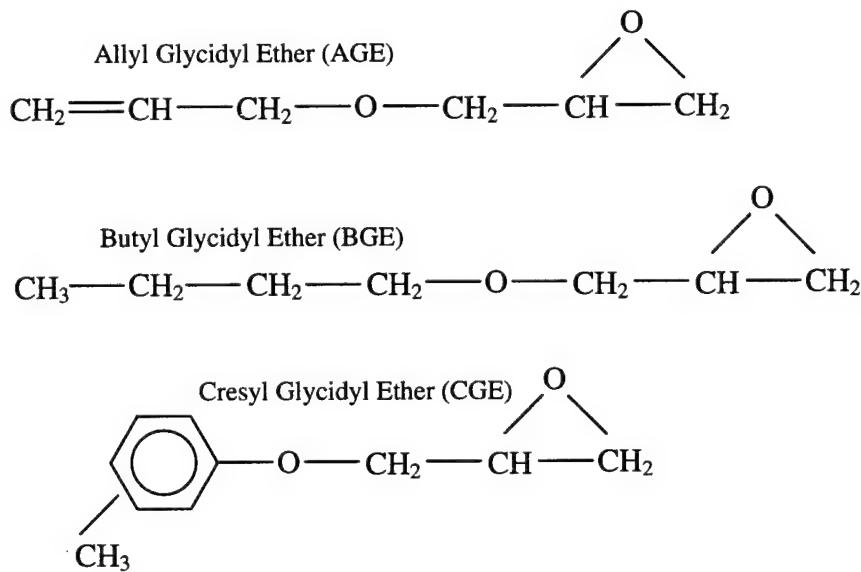


Figure 4
STRUCTURES OF MONOFUNCTIONAL EPOXIDE REACTIVE DILUENTS

This phenomenon may result from the fact that both the epoxy resin and diluent compete for crosslinker in the curing process. If all the diluent does not react with the available curing agent, unreacted material will be present in the coating; the unused diluent becomes trapped by the forming polymer matrix. This scenario is compounded by the addition of twice the recommended amount of reactive diluent. Since the diluent is capable of reacting with the curing

agent at only one end (monofunctional), there will be "broken" crosslinks interspersed throughout the polymer matrix. Any unreacted materials would have a clear path to migrate to the surface and produce the conditions previously described.

Additional epoxy topcoats were formulated with a difunctional reactive diluent: neopentyl glycol, diglycidyl ether. Its structure is shown in figure 5. It was postulated that if a similar situation occurred in coatings formulated with NGDE as that which occurred in those formulated with the monofunctional diluents, there would be no "broken" crosslinks since the diluent is capable of reacting at both ends. If any material were to remain unreacted, most would become trapped in the polymer matrix because diffusion to the surface would be more difficult. Its hydrophilic structure can result in binding water molecules bound for the coating/metal interface.

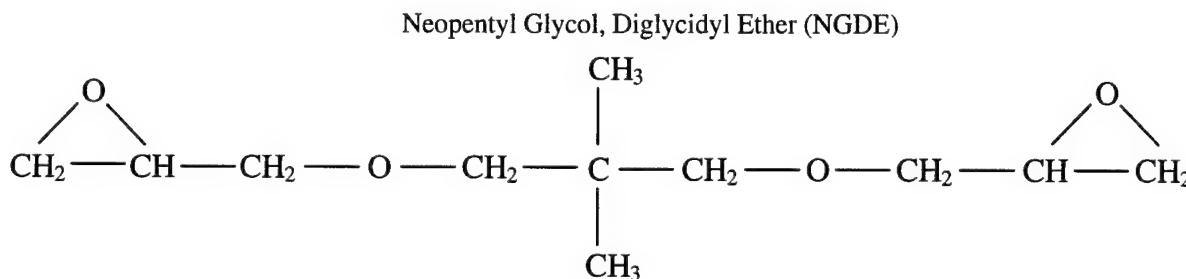


Figure 5
STRUCTURE OF THE DIFUNCTIONAL REACTIVE DILUENT NGDE

The first coatings formulated with NGDE passed most of the requirements of Military Specification MIL-C-22750. Deficiencies were observed in the film quality (seen as orange peel), which resulted in nonreproducible gloss values. It was also determined that the optimum properties of the epoxy topcoats were produced when a stoichiometric excess in curing agent was used. This result is most likely due to two factors: (1) an excess of curing agent will force the epoxy/polyamide reaction to further completion (Le Châtelier's principle) and (2) excess curing agent contains long hydrocarbon chains that are hydrophobic and act as water barriers. However, this curing agent excess resulted in unacceptably short pot lives.

Later formulations containing NGDE were prepared with a TiO₂ dispersion to improve film quality. The TiO₂ is dispersed in a modified thermoplastic acrylic with a blend of solvents. Use of the dispersion resulted in consistently higher gloss readings. Also, pot life was increased to an acceptable value because of the longer-drying solvents present in the dispersion.

An epoxy topcoat meeting all the requirements of the MIL-C-22750 specification was developed and is shown as the sample epoxy formulation in table 2. Similar results were observed when a modified DGEBA resin (DER 660-PA80, Dow Chemical Co.) was substituted for the original DGEBA epoxy resin. The results of the testing are given in table 3, along with the results of the control formulation. In this document, the two systems will be referred to as epoxy topcoats A and B, respectively.

Table 3
TESTING RESULTS (MIL-C-22750) FOR EPOXY TOPCOATS A, B, AND CONTROL

Test Name	Topcoat A	Topcoat B	Control	Required
<u>Adhesion</u>				
Dry Scrape (kg)	6.5	6.5	6.0	≥3
Dry Tape ("A" Method)	4A	4A	4A	≥4A
Wet Tape (24 hr / Room Temp.)	4A	4A	4A	≥4A
Wet Tape (4 days / 120°F)	4A	4A	4A	No Requirement
Wet Tape (7 days / 150°F)	3A	3A	4A	No Requirement
<u>Fluid / Heat / Weather Resistance</u>				
Water Resistance (24 hr / RT)	Pass	Pass	Fail	Pass
Water Resistance (4 days / 120°F)	Pass	Pass	Fail	No Requirement
Water Resistance (7 days / 150°F)	Fail	Fail	Fail	No Requirement
MIL-L-23699 Oil (24 hr / 250°F)	Pass	Pass	Pass	Pass
MIL-H-83282 Hydraulic (24 hr / 150°F)	Pass	Pass	Pass	Pass
Hydrocarbon JP-5 (7 days / RT)	Pass	Pass	Pass	Pass
Methyl Ethyl Ketone Resistance	Pass	Pass	Pass	Pass
Heat Resistance (1 hr / 250°F)	Pass	Pass	Pass	Pass
Weatherometer (500 hr)	Pass	Pass	Fail	Pass
<u>Flexibility</u>				
GE Impact (% Elongation, RT)	5	2	1	No Requirement
Mandrel Bend (in., RT)	0.250	0.375	0.250	≤1
<u>Miscellaneous</u>				
VOC (g/l)	340	340	565	≤340
Admix Viscosity (Sec. Through No. 4 Ford Cup)	32	29	14	≤60
Pot Life (Viscosity after 4 hr)	75	78	19	≤80
Dry Hard Time (hr)	<8	<8	<8	≤8
Gloss at 60 deg Incidence (% Reflected)	91	90	96	≥90
Gloss at 85 deg Incidence (% Reflected)	97	94	88	No Requirement
Strippability (% Removed)	100	100	100	≥90
Cleanability (% Cleaned)	48.4	64.3	83.3	No Requirement

Epoxy topcoats were also formulated with a DGEBF resin. DGEBF resins exhibit significantly lower viscosities as their DGEBA counterparts at 100% solids; this phenomenon was discussed earlier in this document. Coatings containing DGEBF were found to have very similar properties as those containing DGEBA, including a low admix viscosity and excellent pot life. However, resins based on DGEBF are cloudy, and their incorporation into coatings results in very low gloss

readings, even when the pigment dispersion was used. The focus of this paper was the formulation of high-gloss topcoats; therefore, work with the DGEBF coatings was discontinued. DGEBF resins may be useful in low VOC epoxy topcoats where low gloss is required, e.g., camouflage coatings.

Three attempts were made at improving the 7 days / 150°F adhesion and water resistance of epoxy topcoat A. Although MIL-C-22750 does not require the coating to stand up to these conditions, the ultimate goal here is to develop superior coatings for aerospace purposes. The first attempt at improvement involved the substitution of a long-chain flexibilizer/diluent (NC-513, Cardolite Corp.) for NGDE. No significant improvements were observed; however, pot life was reduced to an unacceptable value. The second and third attempts substituted the polyamide curing agent with a phenalkamine material (NC-541X90, Cardolite Corp.) and a 50/50 mixture of polyamide/phenalkamine (based on solids), respectively. The phenalkamine curing agent was designed to resist water by incorporating hydrophobic long-chain alkyl groups and aromatic rings into the polymer matrix. It also imparts flexibility and rapid cure with good pot life. Both attempts showed slight improvements in flexibility, but no improvements in water resistance. Also, weatherability and heat resistance were lost, most likely due to the high aromatic content of the resin. These failed attempts, along with the high yellow content of films cured with the Cardolite materials (both NC-513LC and NC-541X90 have a very dark orange color), resulted in the discontinuation of formulating with these materials.

Despite the failed attempts at improving adhesion during immersion in water at elevated temperatures, a gloss-white epoxy topcoat was developed. The coating met all the requirements of the MIL-C-22750 specification and performed well in some nonspecification tests as well. The new epoxy topcoat exhibited superior performance to the control formulation while reducing VOC's by 40%.

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